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Ultraviolet Spectrophotometric Simultaneous Determination of Iron, Lead, and Bismuth by Perchloric Acid

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The ultraviolet spectrophotometric determination of iron, lead, and bismuth was studied. In the perchloric acid medium these metals exist as hydrated aquo ion. The absorption spectra were obtained with maximum at 208 mμ, (Pb), 222 mμ (Bi), and 240 mμ (Fe), respectively. The calibration curve was made for each element at the above wave lengths using the perchloric acid as reagent. For the mixed sample solutions of iron, lead, and bismuth in various concentrations, the simultaneous determination was made by measuring the absorbancies at three wave lengths. The mean errors for the determination were 0.6 % for iron, 4.5 % for lead, and 2.2 % for bismuth, respectively, in the range of 2.5–12.5 p.p.m. in various concentrations. The proposed method of determination of these elements is simple in procedure and has a high sensitivity comparable to that of other common spectrophotometric or colorimetric method.

The absorptiometric determination of metals using various mineral acids as reagents is convenient and useful in that no special reagents such as organic reagents are needed.

Several works have been recently reported about the methods using mineral acids such as hydrochloric[1], hydrobromic[2)~5)], and sulfuric acid[6)]. In the studies to establish a series of the ultraviolet spectrophotometric determinations of metallic ions, we have already reported the methods for determining iron (III), lead, and bismuth in which sulfuric[7)], perchloric[8)~10)], hydrochloric[11)12)], and acetic acids[13)] were used as reagents respectively.

In these methods, absorptions due to the complexes formed between these metallic ions and simple anions such as sulfate, hydroxyl, chloride, and acetate ions were measured. In these cases, however, appreciable interferences were found when the above metals coexisted. Therefore, it seemed more favourable to establish a method of determination of these metals simultaneously.

The present paper deals with the study on simultaneous determination of iron, lead, and bismuth by ultraviolet absorptiometry using perchloric acid as a reagent.

EXPERIMENTAL AND RESULTS

1. Apparatus and Materials. Spectrophotometric measurements were made with a Beckman Quartz Spectrophotometer, Model DU, with 1 cm. silica transmission cells.

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The stock solution of iron (III) was prepared as follows : Ferric perchlorate was formed by dissolving proper amounts of electrolytic iron in perchloric acid (about 4 N), oxidizing by hydrogen peroxide (30 %), and evaporating the solution until the crystals appear. After perchloric acid was added to dissolve the deposit, the solution was evaporated again. The procedure was repeated until the solution gave negative test for chloride and iron (II) ions. Resulting solution was diluted with dilute perchloric acid to the concentration of 1,000 p.p.m. All the solutions for absorbance measurement were prepared by diluting the required quantity of the stock solution.

The stock solutions of lead and bismuth were prepared respectively from lead acetate and metallic bismuth by the above-described method for the solution of iron.

Absorbance measurement for each solution was as follows : Aliquot amount of the above metallic stock solutions was pipetted into the volumetric flask. The proper amount of perchloric acid was added, and it was then diluted to the concentration of 10.0 p.p.m. by distilled water. The final acidity was 1 N for the perchloric acid. After thorough mixing, the absorbancy was measured using 1 N perchloric acid as a reference.

2. Absorption Spectra. In the perchloric acid medium, aquo-complexes of iron, lead and bismuth are formed, the absorption spectra being shown in Fig. 1.

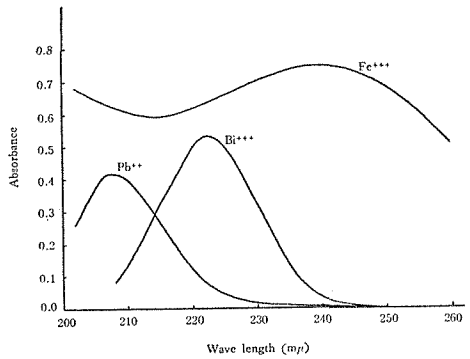

Fig. 1. Absorption curves of Fe^{+++}, Pb^{++} and Bi^{+++}.
Concentration of metallic ions ; 10.0 p.p.m.
Concentration of perchloric acid ; 1 N.

In these cases, since the absorbancies of these spectra vary slightly with the perchloric acid concentrations, the concentration of perchloric acid in the sample solutions should be held constant. In this experiment all measurements were made for 1 N perchloric acid solutions.

For the simultaneous determination of these three elements the following seven wave lengths were selected ; the three wave lengths of each absorption peak for three elements (Fe : 240 mμ, Pb : 208 mμ, Bi : 222 mμ), two wave lengths which show similar order of sensitivity for lead and bismuth (214 mμ and 217 mμ), and two wave lengths (255 mμ and 260 mμ) in which the absorbancies of lead and bismuth are very slight although sensitivity for iron decreases.

The calibration curves were made for these seven wave lengths by measuring the absorbancies of above metals each for such concentrations as 2.5, 5.0, 7.5, 10.0, 15.0 and 20.0 p.p.m.

Results are shown in Fig. 2. Beer's law is followed in the range 0.25-20.0 p.p.m. in all cases.

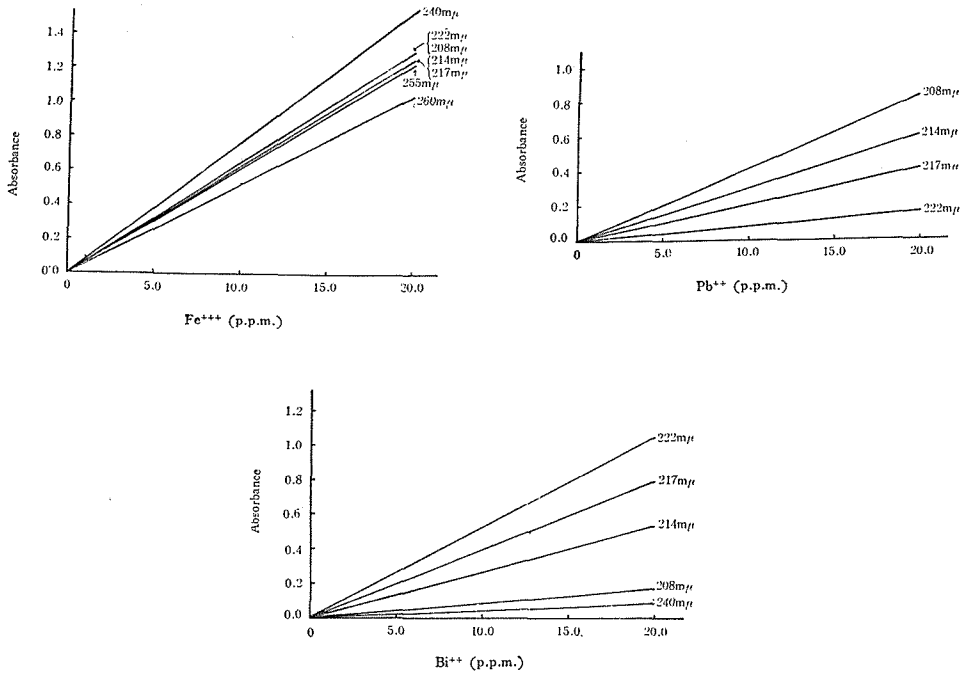

Fig. 2. Calibration Curves of Fe^{+++}, Pb^{++} and Bi^{+++}.
Concentration of perchloric acid ; 1 N.
Reference ; 1 N. $HClO_4$.

3. Simultaneous determination. For the purpose of simultaneous determination of iron, lead and bismuth, each absorbance indices should be evaluated from the absorbancies given in the calibration curves at each of the seven wave lengths. The absorbance indices given here are not the molar extinction coefficients but, for convenience in calculation, are arbitrary constants relating absorbance to the

Table 1. Absorbance indices at various wave lengths.

Wave Length (mμ)	Fe	Pb	Bi
208	0.0640	0.0422	0.0079
214	0.0622	0.0308	0.0264
217	0.0618	0.0210	0.0393
222	0.0644	0.0083	0.0520
240	0.0748	——	0.0039
255	0.0611	——	——
260	0.0516	——	——

Table 2. Simultaneous determination of Fe^{+++}, Pb^{++}, Bi^{+++} by perchloric acid.

Present (p.p.m.)			Fe^{+++} Found (p.p.m.)		Pb^{++} Fonnd (p.p.m.)						Bi^{+++} Found (p.p.m.)						
Fe^{+++}	Pb^{++}	Bi^{+++}	255 mμ	260 mμ	208 mμ 214 mμ	208 mμ 217 mμ	208 mμ 222 mμ	214 mμ 217 mμ	214 mμ 222 mμ	217 mμ 222 mμ	240 mμ	208 mμ 214 mμ	208 mμ 217 mμ	208 mμ 222 mμ	214 mμ 217 mμ	214 mμ 222 mμ	217 mμ 222 mμ
7.50	7.50	7.50	7.58	7.56	7.87	7.79	7.76	7.27	7.28	7.34	6.67	6.85	7.26	7.44	7.54	7.79	7.50
5.00	5.00	5.00	5.06	5.04	5.23	5.18	5.16	4.86	4.88	4.91	5.64	4.58	4.84	4.94	5.01	4.99	4.99
7.50	2.50	7.50	7.51	7.50	2.65	2.59	2.56	2.21	2.19	2.03	6.92	6.98	7.29	7.46	7.49	7.50	7.72
7.50	7.50	2.50	7.51	7.54	7.30	7.24	7.24	6.87	7.04	7.31	1.03	2.17	2.47	2.44	2.66	2.47	2.43
2.50	7.50	7.50	2.50	2.48	7.51	7.48	7.47	7.29	7.30	7.31	8.21	7.22	7.38	7.44	7.48	7.45	7.47
12.50	2.50	2.50	12.36	12.38	2.13	2.09	2.11	1.79	2.03	2.42	0.77	2.29	2.52	2.39	2.68	2.41	2.34
2.50	2.50	12.50	2.52	2.52	2.81	2.81	2.80	2.77	2.72	2.68	12.05	12.44	12.47	12.53	12.49	12.55	12.56
2.50	12.50	2.50	2.47	2.44	12.15	12.16	12.14	12.18	12.10	11.98	3.08	2.30	2.28	2.35	2.27	2.36	2.38
10.00	2.50	5.00	9.93	9.90	2.27	2.22	2.43	1.84	2.14	2.64	3.33	4.70	5.00	5.22	5.20	4.85	4.77
10.00	5.00	2.50	9.96	9.96	4.80	4.73	4.73	4.31	4.47	4.72	0.51	2.09	2.43	2.44	2.66	2.48	2.44
5.00	2.50	10.00	5.02	4.92	2.62	2.59	2.59	2.42	2.46	2.52	10.26	9.67	9.81	9.84	9.90	9.86	9.85
2.50	5.00	10.00	2.47	2.50	5.27	5.16	5.16	5.00	5.09	5.23	9.23	9.79	9.92	9.89	10.00	9.90	9.88
5.00	10.00	2.50	4.99	5.02	9.70	9.68	9.68	9.51	9.61	9.76	0.77	2.36	2.49	2.45	2.58	2.47	2.44
2.50	10.00	5.00	2.49	2.48	9.81	9.84	9.82	9.92	9.85	9.63	5.38	4.91	4.79	4.87	4.72	4.87	4.91
Mean of error per cent			0.6	0.8	5.5	5.3	4.5	8.5	6.5	4.5	27.5	6.6	2.3	2.2	3.2	1.8	2.3

concentration in parts per million at the fixed path lengths of the cells used in the measurements. These are given in Table 1. For the 14 mixed sample solutions of iron, lead, and bismuth in various concentrations, the concentrations of these elements were determined in parts per million by solving the simultaneous equations corresponding to the above wave lengths. Results are shown in Table 2, the mean errors being also tabulated in per cet.

As shown in Table 2, the following facts can be seen : In the determination of iron, the mean error in per cent is somewhat less at 255 mμ than at 260 mμ. As to the determination of lead, the result calculated using simultaneous equations for 208 mμ/222 mμ is minimum in error, and the same value was obtained for 217 mμ/222 mμ. In the case of bismuth, the results show 1.8% mean error at 214 mμ/222 mμ and 2.2% at 208 mμ/222 mμ. Consequently, in the simultaneous determination of lead and bismuth the pair of wave lengths of 208 mμ and 222 mμ must be selected because the sum of per cent mean errors of both elements is minimum.

Based on these results, following method is proposed for the simultaneous determination of mixed solution of iron, lead, and bismuth.

First, the absorbance of the sample solution is measured at 255 mμ, and from this value the concentration of iron is calculated in parts per million. At this wave length, absorbancies for lead and bismuth are negligibly small. Next at 208 mμ and 222 mμ the absorbancies of mixed sample solutions are measured, and from these values the absorbancies of iron for both wave lengths calculated from iron content obtained at 255 mμ are subtracted. Then, from the remaining absorbancies at both wave lengths, lead and bismuth are determined respectively by means of simultaneous equations.

The mean errors of the determination were 0.6% for iron, 4.5%, and 2.2% for lead and bismuth respectively in the range of 2.5-12.5 p.p.m. in various concentrations.

SUMMARY

In the mixed sample solution of iron, lead and bismuth, concentration of each was calculated in parts per million from the absorbance measurements at the appropriate wave lengths.

All the results of determination of these elements in various mixed sample solutions were found to be in good agreement with theoretical value within the error of several per cent.

The proposed method of determination of these elements is simple, convenient, and has a sensitivity comparable to that of other common spectrophotometric or colorimetric methods.

The use of perchloric acid may be superior to other reagents since it is a more common reagent and lower in cost.

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